

Investigation of Si₃N₄ Ceramic/42CrMo Steel Joints Brazed with Ag-Cu-Ti Brazing Alloy Plus WC Particles

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Abstract

Active metal brazing is a widely used technique to join advanced ceramics and metals. In this research, Ag-Cu-Ti+WC composite filler was employed for the joining of Si₃N₄ ceramic and 42CrMo steel. Effect of WC particles content on the microstructure and mechanical properties of the joints was investigated. The results indicated that a continuous reaction layer was formed at the substrates/brazing alloy interface. The brazing layer was mainly composed of Ag and Cu based solid solution, in which WC particles, TiC reaction layer around WC and Cu-Ti intermetallics were randomly dispersed. The maximal bending strength could reach 320.5 MPa while 15 vol.% WC particles were incorporated, in which the joint strength was 180.65% higher than the average strength for the case without WC particles addition. The following factors cooperated together to contribute the maximum: the coefficient of thermal expansion reduction of the brazing alloy, formation of Cu-Ti intermetallics, the reaction layer with a definite thickness formed at the Si₃N₄ ceramic/brazing alloy interface.

Keywords

Si₃N₄ Ceramic; Joining; Inclusions; Residual Stress; Mechanical Properties

Introduction

Silicon nitride ceramics exhibit excellent mechanical properties in harsh environments, such as high strength, Young's modulus, hardness, corrosion and wear resistance, and have shown increasing use in the wide engineering applications (Blugan et al, 2004). Similar to most ceramics, silicon nitride is difficult to be produced into complex or large workpieces due to its natural brittleness, restricting its wide use. Although metals or alloys, especially steel, tend to possess different properties, such as good plasticity and toughness, easy fabricability and electrical conductivity, they generally lack the corrosion resistance and high durability of ceramics. To full use

of respective advantages of ceramics and metals, it is necessary to join the ceramics with metallic parts. There are many applications in which both ceramics and steel can be employed to maximize the performance and minimize the respective shortcoming, such as heat exchanges, cutting tools, articular prostheses and so on (Liu et al, 2010). In the past, the researches with regard to the bonding technologies of ceramics and metals have been well investigated. Among them, brazing has received far-ranging attention due to its convenience and cost-effectiveness (Xian et al, 1990; Zhang et al, 2010).

Two main problems will occur when joining ceramics to metals: the first is the poor wettability of ceramics by most metals or alloys, which can be overcome by use of an active filler alloy. The active element in the filler alloy, such as Ti, Zr, has sufficient thermodynamic driving force to destabilize the ionic or covalent bonding in the ceramics by reacting with one or more elements in the ceramic. The second problem is the significant differences in the physical and mechanical properties among the ceramic, metal and brazing alloy, such as coefficients of thermal expansion (CTE) and Young's moduli. These differences can lead to high residual stresses when cooling from the brazing temperature, leading to the component fracture under a low load (Blugan et al, 2007; Xu et al, 1994; Park et al, 2004; Park et al, 2002).

The commercial Ag-Cu-Ti brazing alloy has been widely introduced for the joining of ceramic and metal, and it displays good wettability to most of ceramics (Liu et al, 2006). However, the CTE of Si₃N₄ ceramic is $3 \times 10^{-6} \text{ K}^{-1}$ and that of 42CrMo steel is $11.1 \times 10^{-6} \text{ K}^{-1}$, but the CTE for Ag-Cu-Ti is $18 \times 10^{-6} \text{ K}^{-1}$. Thus, a large residual stress is inevitably induced. In order to fix the problem, lots of researchers have reported that the materials with a low CTE (particles or fibers) could be

incorporated in the brazing alloy, thus the CTE of brazing alloy was reduced and the joint strength was accordingly improved (Buhl et al, 2000; Lin et al, 2006; Wielage et al, 2007; Qin et al, 2010; Zhu et al, 1997; Lin et al, 2007; Yang et al, 2005; Lin et al, 2006; Yang et al, 2011; He et al, 2011; Lin et al, 2011; Yang et al, 2011; Yang et al, 2012; Yang et al, 2012; He et al, 2012; Yang et al, 2012). Our research group has introduced the SiC or Mo particles-reinforced active brazing alloy to join Si₃N₄ ceramic and the joint strength was also greatly improved (He et al, 2010; He et al, 2011). In the investigation, a definite amount of WC particles (5-20 vol.%) whose CTE was only $5.1 \times 10^{-6} \text{ K}^{-1}$ was incorporated into Ag-Cu-Ti for the joining of Si₃N₄ ceramic and 42CrMo steel. The CTE reduction of the composite filler (Ag-Cu-Ti+WC) could be achieved due to WCp (p=particle) addition. Meanwhile, WCp can also strengthen the brazing alloy owing to its high strength and hardness. On that basis, effect of WCp content on the microstructure and mechanical properties of the joints was investigated.

Materials and Methods

The Si₃N₄ ceramic used in the research was hot pressed. The metal partner was 42CrMo steel with the following chemical compositions: Fe-0.42C-1.0Cr-0.7Mn-0.3Si-0.5Mo (wt.%). The ceramics and steels were sliced into 3 mm × 4 mm × 17 mm pieces for bending test. The brazing surfaces (3 mm × 4 mm) of ceramics were coarsely ground on silicon carbide paper down to 1200 grit and then polished with 1 μm diamond paste. Meanwhile, the brazing surfaces (3 mm × 4 mm) of the steel were ground by using silicon carbide paper of 600, 800 and 1200 grit one after another. The composite filler was composed of 69.12Ag-26.88Cu-4Ti (wt.%) alloy powder with an average diameter of 50 μm and WC particles with an average particle size of 10 μm. On the basis of our previous work (He et al, 2010; He et al, 2011), WCp with small size (<10 μm) was not selected since it is difficult to segregate the small size WCp with Ag-Cu-Ti powders uniformly during preparation. The WCp with large size (>10 μm) was also abandoned. The composite filler with large size WCp addition will not effectively reduce the CTE because the large WCp does not disperse evenly in the joint. The volume fraction of WCp in the composite filler was set at 0%, 5%, 10%, 15%, 20% and 25%. The initial powder mixtures were high-power ball milled for 2 hours in vacuum with a ball (Al₂O₃) to powder mass ratio of 10:1 and rotation speed of 150 r/min. After that, a small amount of binder was added into the mixture

for making a composite paste. Before assembling, the Si₃N₄ ceramics and 42CrMo steels were cleaned with acetone in an ultrasonic bath for 30 minutes. Then, the composite paste was placed between Si₃N₄ ceramic and 42CrMo steel, then, the assembly was placed in a special brazing jig to align the ceramic and metal specimens and a normal load of 0.015 MPa was applied on the assembly. During brazing, the assembly was heated to 573 K at a rate of 10 K/min and held for 30 min to make the organic glue volatilize. Further, the temperature increased to 1173 K at a rate of 10 K/min and held for 10min. At last, the sample was cooled at a rate of 5 K/min to 473 K and then cooled in the furnace without power. It should be noted that the vacuum in the furnace should be kept below $3 \times 10^{-3} \text{ Pa}$ during the process.

The three-point bending tests were carried out by Instron-5569. Fig. 1 schematically clarified the three-point bending tests. The specimen dimension was 3 mm × 4 mm × 34 mm, and the direct loading position was the brazing seam. In addition, the distance between the supports was set at 30 mm. During test, the load was applied on the brazing seam gradually with a cross-head speed of 0.5 mm/min until the butt-joint fractured. At least three samples were used to determine the bending strength for each joining condition. The cross-sections of the brazed joints were cut and polished with 1 μm diamond paste, and examined by means of scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). In addition, the phases in the joints were identified by an X-ray diffraction (XRD) method.

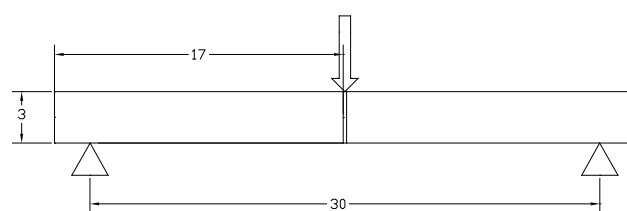


FIG. 1 CONFIGURATION FOR THREE-POINT BENDING TESTS

Results and Discussion

Microstructure of the Si₃N₄/42CrMo Steel Joints

Fig. 2 displays the SEM images for initial Ag-Cu-Ti, WC powders and the mixed powder after 2 hours mechanical alloying. By examining the morphology of mixed powder, most of the Ag-Cu-Ti powder showed neglectable variation while partial Ag-Cu-Ti with small size was deformed from pellet to disk. In addition, WC was conglomerated on the Ag-Cu-Ti powder after mixing.

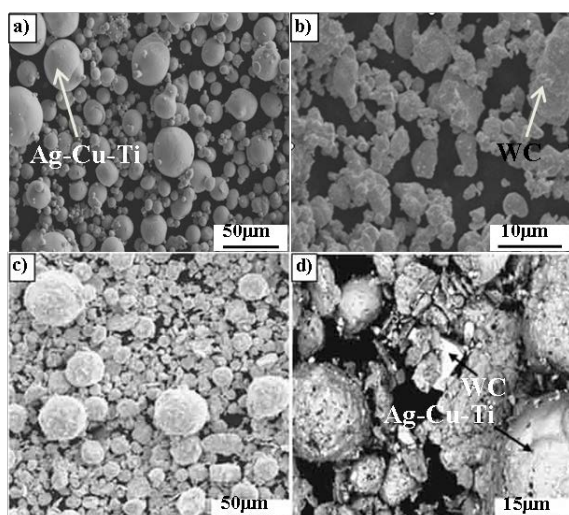


FIG. 2 SEM MICROGRAPHS OF THE Ag-Cu-Ti+WCp COMPOSITE FILLER: (a) INITIAL Ag-Cu-Ti POWDER; (b) INITIAL WCp; (c) MIXED Ag-Cu-Ti+WCp POWDER AFTER MECHANICAL ALLOYING; (d) MAGNIFIED AREA IN MIXED POWDER

Fig. 3 shows the back-scattered micrograph and elementary distribution in a $\text{Si}_3\text{N}_4/42\text{CrMo}$ joint brazed with Ag-Cu-Ti+15vol.% WCp composite filler. As shown in the picture, the composite filler shows good wetting to the substrates. WC is homogeneously dispersed in the joint. In addition to that, a distinct reaction layer was formed at each side of substrates, as demonstrated by arrow A and B in Fig. 3. The reaction layers are mainly composed of Ti element (shown in Fig. 3e), indicating that the active Ti element was reacted with the substrates. Actually, the active Ti element diffused towards and reacted with Si_3N_4 ceramic to form TiN reaction layer at the Si_3N_4 ceramic/brazing alloy interface during brazing. During the formation of TiN reaction layer, Si element was released and diffused through the TiN layer into the molten braze. One may speculate that Ti_5Si_3 could be formed near the TiN layer due to the released Si and Ti element with a high concentration near the interface. The gap was excluded from detection between TiN and Ti_5Si_3 layer in Fig. 3(e) since they contacted closely. In another preparing paper, the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was utilized to clarify the elementary distribution characteristics at the interface, and the results showed that there was a Si element diffusing tail penetrating into the TiN layer and N element was also maintained in the Ti_5Si_3 layer, giving us a hint that they are close contact. The above remarkable phenomenon was associated with the following elementary diffusion trend: Ti element diffused toward the $\text{Si}_3\text{N}_4/\text{TiN}$ interface and reacted with Si_3N_4 ; N element diffused through the TiN/ Ti_5Si_3 interface and reacted with Ti; the released Si would diffuse

toward the brazing alloy. The same conclusions were also confirmed by other researches (Subramanian et al, 1993; Lemus et al, 2003; Zhang et al, 2004; Brochu et al, 2005).

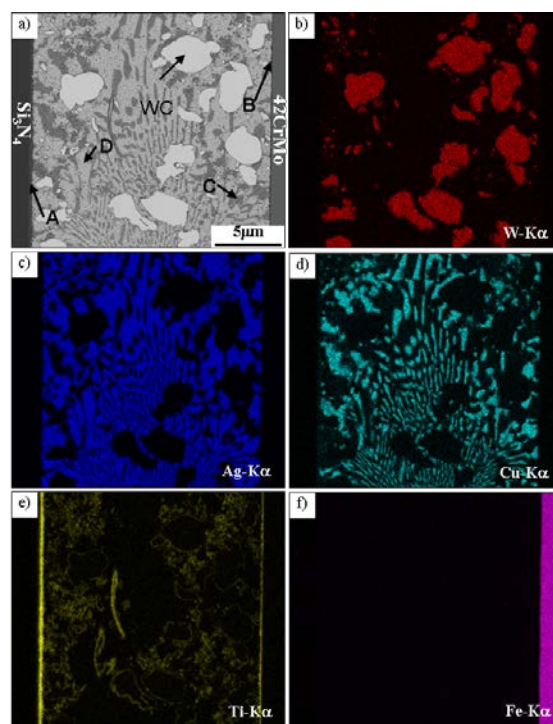


FIG. 3 MORPHOLOGY AND ELEMENTAL ANALYSIS RESULTS OF THE $\text{Si}_3\text{N}_4/42\text{CrMo}$ STEEL JOINT BRAZED USING Ag-Cu-Ti+15VOL.%WCp COMPOSITE FILLER

At the 42CrMo steel/braze interface, the reaction layer with double structure was also observed. The thin Fe_2Ti reaction layer was located near the 42CrMo steel, while the thick FeTi layer was formed near the brazing layer. The EDS analysis indicated that the compositions for them were as followings: $\text{Ag}_{2.0}\text{Ti}_{18.7}\text{Fe}_{72.8}\text{Cu}_{6.5}$ (at.%) and $\text{Ag}_{3.7}\text{Ti}_{40.0}\text{Fe}_{45.2}\text{Cu}_{11.1}$ (at.%). The similar structure was also reported (Ghosh et al, 2005). The grey area C in the joint was composed of $\text{Cu}_{97.8}\text{Ag}_{2.2}$ (at.%), and determined to be Cu based solid solution, in which a definite amount of Ag element (1-10 wt.%) was dissolved. Another main component D, which consists of $\text{Ag}_{77.8}\text{Cu}_{22.2}$ (at.%), was namely Ag based solid solution.

As it can be seen from Fig. 3(e) that Ti element was not only enriched at the interface, but also distributed in the brazing layer. There is a firm evidence that WCp could interact with Ti element during brazing, resulting in a TiC layer surrounding them. In addition, there is a band that has low content of Ti element in the central region compared to the sides, which can be explained by classical composite theory (Dutta et al, 1998; Asthana et al, 1993). The distribution of WCp in the Ag and Cu matrix made the joint appear as a metal

matrix reinforced by particles. Actually, the particle segregation during composite solidification was studied extensively. The lower thermal conductivity of Si_3N_4 ceramic compared to 42CrMo steel would lead to retention of heat in themselves and hence their temperature should be higher than that of steel during solidification. A negative temperature gradient was thus formed from the ceramic to steel in the joint. Once the nuclei were formed in the melt, they would grow towards 42CrMo steel. It is easily understood that the advancing solid-liquid interface interacted with the suspended particles and the interface could either engulf the particles or push them ahead. For a given growth velocity, there had a critical particle size, and the particles larger than the critical size were engulfed by the interface. When the particles were smaller than the critical size, a long range particle pushing could take place, leading to macrosegregation of particles in the solidified composite. So, the particles with larger particles size (such as WCp) would be engulfed by the molten braze. However, the smaller size particles would be pushed towards the sides, such as tiny Cu-Ti intermetallics, leaving the band with a low content of Ti in the central region.

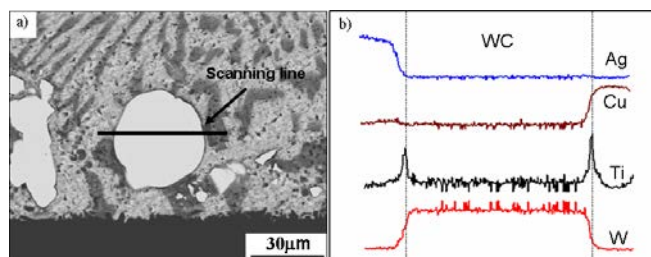
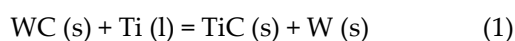


FIG. 4 MORPHOLOGY OF THE JOINT (A) AND LINE SCANNING PROFILES OF W, Ag, Cu AND Ti ELEMENT ACROSS THE BLACK LINE IN (A)

When Ag-Cu-Ti brazing alloy melted during brazing, WC particles kept in solid state. Most importantly, the surface of WCp and Ag-Cu-Ti could interact to a certain extent, introducing new phases. The CTE of the composite filler was thus altered and the joint strength was correspondingly affected. Fig. 4 presents back-scattered micrograph of reaction products in the joint and the line profiles across WCp. The interface between them shows intimate bonding. It is important to note that Ti was enriched WCp/matrix interface, as demonstrated in Fig. 4(b). Based on the thermodynamic information, TiC would be formed when WC particles got in contact with the liquid Ti element by the following reaction:



$$\Delta G \text{ (KJ/mol)} = -213.648 + 0.01079T$$

Estimate of Gibbs free energy has indicated that the

above reaction could occur spontaneously during brazing. The reaction (1) could proceed until the TiC reaction layer with a thickness of 0.1 μm was obtained, impeding Ti diffusing towards WCp further. Similarly, the same results were also reported by previous researches (Li et al, 2009; Chen et al, 2009). The key point some authors also indicated is that the extraction of C from WC may degrade partial WC to W_2C . However, W_2C reaction phases around WC were not detected in the research, which may be caused by the low brazing temperature (1173 K). Actually, the temperature in our research was far lower than that introduced in the previous researches (Li et al, 2009; Chen et al, 2009; Vreeling et al, 2002).

Fig. 5 presents SEM images in the brazing layer. The tiny precipitates were randomly distributed in the brazing layer. The precipitate, such as A, is composed of $\text{Ag}_{16.6}\text{Cu}_{43.6}\text{Ti}_{39.8}$ (at.%) according to EDS results. The stoichiometric ratio between Cu and Ti of the precipitate indicated that it is close to CuTi intermetallic. In addition to that, there were also Cu_4Ti_3 (labeled B: $\text{Cu}_{56.3}\text{Ti}_{43.7}$ (at.)) and Cu_3Ti_2 (labeled C: $\text{Ag}_{3.7}\text{Cu}_{58.5}\text{Ti}_{37.8}$ (at.)) intermetallics detected in the joint. Based on Ag-Cu-Ti ternary phase diagram (Okamoto et al, 1995), Ti began to be dissolved in the Ag-Cu melt when the heating temperature reached 1053 K. At 1123 K, the whole Ag-Cu-Ti was in liquid state while WCp was still solid. Ti diffused towards and reacted with WCp, leading to formation of W reaction phases in the brazing layer. According to W-Ti binary phase diagram (Massalski et al, 1991), Ti has two typical allotropic structures, existing in the form of α -Ti at low temperatures (below 1155.5 K) and transforming to β -Ti above 1155.5 K. Also, and most importantly, β -Ti and W are infinitely miscible theoretically. However, the maximal solubility of W in α -Ti was less than 1.5 wt.% and α -Ti cannot be dissolved in W. Since Ti element in the joint was β -Ti at 1173 K, β -Ti and W could be dissolved mutually since Ti was highly diluted in the brazing alloy and segregated to the WCp surface. However, they were not infinitely miscible due to the presence of a monotectoid transformation. The transformation of β -Ti \rightarrow α -Ti occurred while the temperature was cooled to 1155.5 K. In the subsequent cooling, those Ti dissolved in W were released owing to the lower solubility between α -Ti and W. Attention should be paid to that no segregation of α -Ti took place based on W-Ti binary phase diagram (Massalski et al, 1991). Due to the strong affinity between Ti and Cu, the released Ti element was dissolved in Cu element. Many kinds of Cu-Ti intermetallics were thus precipitated.

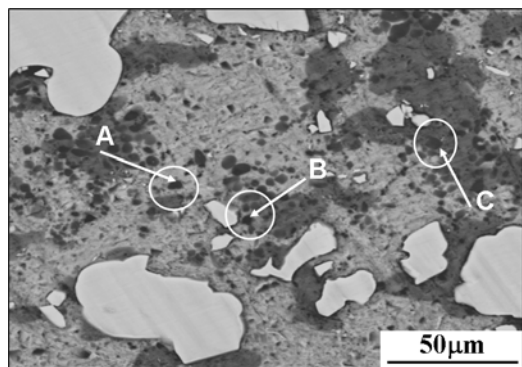


FIG. 5 BACK-SCATTERED ELECTRON IMAGES OF THE $\text{Si}_3\text{N}_4/42\text{CrMo}$ STEEL JOINT BRAZED BY USING Ag-Cu-Ti+15VOL.% WCp COMPOSITE FILLER.

Cu-Ti intermetallics have been observed as well in the joint by TEM analysis, as indicated in Fig. 6.

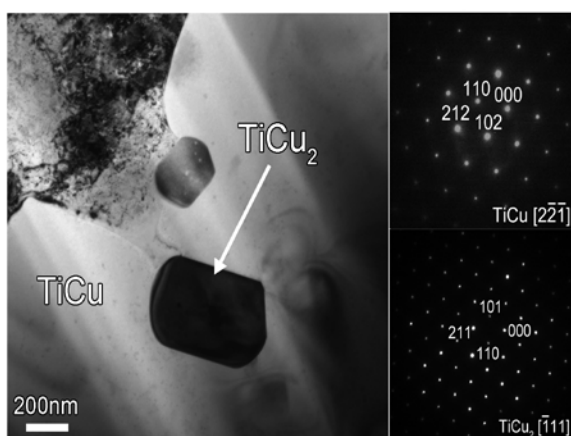


FIG. 6 TEM MORPHOLOGY IN THE JOINT BRAZED WITH Ag-Cu-Ti+Mo COMPOSITE FILLER

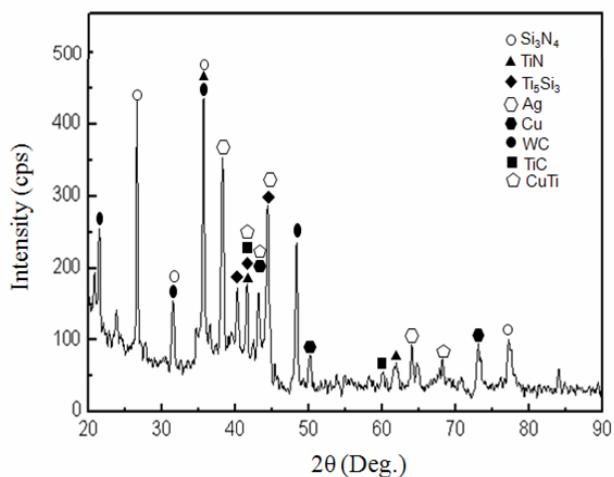


FIG. 7 XRD PATTERNS OF THE BRAZING LAYER (NEAR Si_3N_4 CERAMIC) IN THE JOINT BRAZED WITH Ag-Cu-Ti+15VOL.% WCp COMPOSITE FILLER

X-ray diffraction was performed on the fracture surface after bending test. Fig. 7 shows the XRD pattern of the brazing layer (near Si_3N_4 ceramic) in the joint brazed with Ag-Cu-Ti+15vol.% WCp composite filler. As it can be seen from the picture that TiN, Ti_5Si_3 , WC, TiC and Cu-Ti intermetallics were detected,

meaning that the above deductions with regard to the precipitation of Cu-Ti intermetallics and the reaction between WC and Ti were reasonable.

Effect of WCp Content on Microstructure and Mechanical Properties of the Brazed Joints

Fig. 8 shows SEM micrographs of the Si_3N_4 ceramic/42CrMo joints for the case of mutative content of WCp in the composite filler. A well-bonded joint was always obtained when the content of WCp was increased from 0 vol.% to 25 vol.%. A more striking phenomenon is that more Cu-Ti intermetallics were precipitated with increasing content of WCp in the joint, as demonstrated in Fig. 8(b-f). When the content of WCp was higher, it can be easily inferred that the increased W phases were formed due to the interaction between WCp and Ti. Since Ti elements were highly diluted and segregated to the surface of WC, more Ti element were involved to be dissolved around W, resulting in excess Ti expelled into the brazing layer after the allotropic transformation. That is the key reason for excess Cu-Ti intermetallics precipitating.

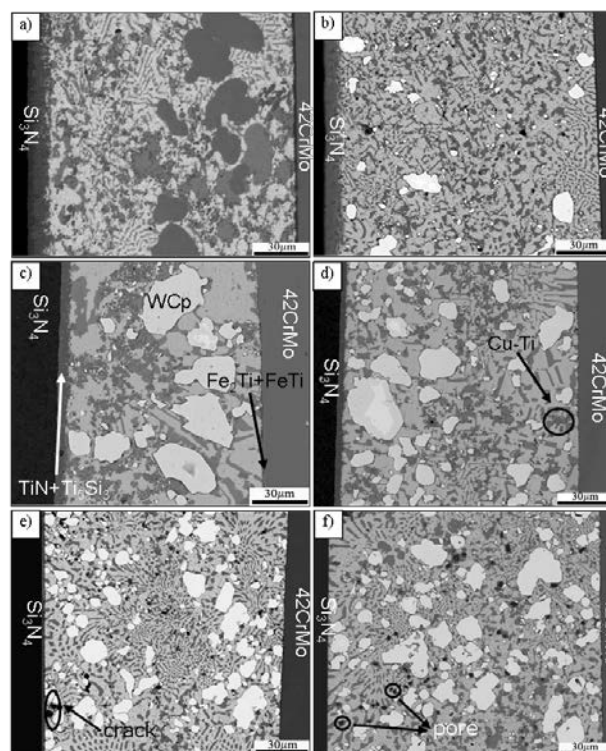


FIG. 8 SEM MICROGRAPHS OF THE Si_3N_4 CERAMIC/42CrMo JOINTS FOR THE CASE OF UNIFORMLY DISTRIBUTED WCp IN THE COMPOSITE FILLER: (A) 0 vol % WCp; (B) 5 vol% WCp; (C) 10 vol% WCp; (D) 15 vol.% WCp; (E) 20 vol.% WCp; (F) 25 vol.% WCp

Another striking phenomenon is that the thickness of interfacial reaction layer decreased with increasing content of WCp in the joint. The thickness of reaction layer (TiN+ Ti_5Si_3) at the Si_3N_4 ceramic/brazing alloy

interface was 4 μm when the content of WCp was 5 vol.%. However, it was only 0.5 μm while the content of WCp was increased to 25 vol.%. In addition to that, the thickness of Fe₂Ti/FeTi reaction layer at the 42CrMo steel/brazing alloy interface behaved the same trend. It should be noted that the content of Ti element was 4 wt.% in all joining conditions. Due to the trapping of Ti by increased WCp, the amounts of Ti element that diffused towards the substrates were accordingly decreased.

Fig. 9 illustrates the three-point bending test results of the Si₃N₄/42CrMo joints brazed with Ag-Cu-Ti+WCp composite filler. The joint strength was only 114.2 MPa while the joint was brazed with Ag-Cu-Ti. Whereas, it increased and then decreased with increasing content of WCp from 5 vol.% to 25 vol.%. The maximal bending strength (320.5 MPa) was obtained while 15 vol.% WCp was incorporated, which was 180.65% higher than the strength for the case without WCp addition. The joint strength decreased sharply with further increasing content of WCp to 20 vol.% or 25 vol.%. However, the joints brazed with Ag-Cu-Ti+WCp were always stronger than those brazed with Ag-Cu-Ti alone.

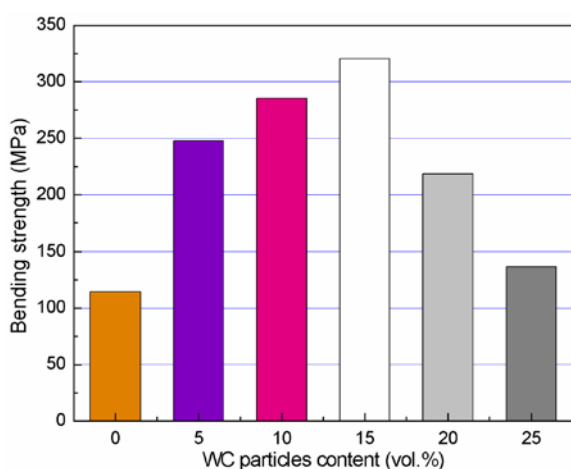


FIG. 9 BENDING STRENGTH VERSUS DIVERSE WCp CONTENT IN THE Ag-Cu-Ti+WCp COMPOSITE FILLER

When the joint was brazed with Ag-Cu-Ti, the joint strength was only 114.2 MPa. By incorporating 5 vol.% or 10 vol.% WCp (whose CTE is only $5.1 \times 10^{-6} \text{K}^{-1}$) in the joint, the CTE reduction of the composite filler could be achieved and accordingly the joint strength was elevated. The maximal flexural strength could achieve 320.5 MPa while incorporating 15 vol.% WCp. The following four reasons contributed to the maximum. Firstly, by incorporating 15 vol.% WCp, WCp with low CTE was dispersed in the Ag and Cu based solid solution, resulting in CTE reduction of the brazing alloy. The degree of CTE reduction was believed to

play a vital role in determining the residual stresses level in a brazed joint which can be estimated by using the well-known Rule of Mixture (ROM). For instance, with the addition of 15 vol.% WCp, the CTE reduction of the brazing alloy could be achieved by 11%, as indicated in Table 1.

TABLE 1 THE CTE AND YIELD STRESSES CHANGES IN THE BRAZING ALLOY DUE TO WCp ADDITION

WC (vol.%)	CTE ($\times 10^{-6} \text{K}^{-1}$)	Fractional CTE Decrease Relative to 0 vol.%WCp (%)	Yield Stress (MPa)	Fractional Yield Stresses Increase Relative to 0 vol.%WCp (%)
0	19	0	230	0
5	18.305	3.7	254.6	10.7
10	17.61	7.3	270.2	17.5
15	16.915	11	284.4	23.7
20	16.22	14.6	298.3	29.7

The following two equations were also introduced to elucidate the relationship between the residual stress and CTE misfit (Zhou et al, 1991):

$$\sigma = \frac{E_I E_{II}}{E_I + E_{II}} \Delta \alpha \Delta T \quad (2)$$

$$\sigma = \sigma_{ly} + (E_{lp} \Delta \alpha \Delta T) \quad (3)$$

In equation (2), where α_I and α_{II} are the thermal expansivity of the metal and ceramic ($\Delta \alpha = \alpha_I - \alpha_{II}$), the temperature change is $\Delta T = T_2 - T_1$, and E_I and E_{II} are the elastic moduli of the metal and ceramic. In equation (3), where E_{lp} is the linear strain hardening coefficient and σ_{ly} is the yield strength of the metal. For fully elastic conditions, apart from the yielding effect in the brazing alloy, the thermal residual stress σ in the joint is determined by equation (2). While the thermal stress in the metal exceeds its yield strength, the determining equation for the thermal stress is expressed by equation (3). However, the thermal stresses always correlates with the CTE misfit among the joined materials in two conditions. With reducing CTE misfit, the residual stress was accordingly lowered. Secondly, the Cu-Ti intermetallics should consume Ti element and decrease the amount of Ti elements that were diffused towards Si₃N₄ ceramic, resulting in the thickness of reaction layer at Si₃N₄ ceramic/braze interface diminished from 11.4 μm at 0vol% WCp to 1.3 μm at 15vol% WCp. It is essential that an interfacial reaction layer was formed (Zhang et al, 2002), since it can decrease the thermal residual stresses gradient between the joined materials. However, the joint strength will also decrease when the thickness of the reaction layer exceeds a certain value ($>1.3 \mu\text{m}$ in the research) because the interfacial reaction products are brittle and show different

thermal expansion coefficient with the matrix. For instance, the CTE for TiN and Ti5Si3 reaction phases are $9.35 \times 10^{-6} \text{ K}^{-1}$ and $11.0 \times 10^{-6} \text{ K}^{-1}$, respectively, both higher than that of Si₃N₄ ceramic ($3 \times 10^{-6} \text{ K}^{-1}$). Due to direct contact, this CTE mismatch could influence the residual stresses level in the joint. In the research, the optimum thickness for the reaction layer at Si₃N₄ ceramic/braze interface was 1.3 μm while the maximal joint strength was obtained. Thirdly, it is beneficial to the joint strength that Cu-Ti intermetallics were dispersed in the joint after brazing due to their lower CTE, which could also lower the CTE of the composite filler. Finally, WCp could increase the strength of the brazing alloy because of its high strength and hardness, improving the strength of soft metallic brazing layer and strengthening its load-carrying capacity. The above four factors cooperated together to improve the joint strength.

With incorporating the content of WCp over 15 vol.%, the joint strength tended to decrease. An abundant WCp and brittle Cu-Ti intermetallics were present in the joint, limiting the ability of Ag and Cu based solid solution to plastic deformation. We have introduced the equation (Zhang et al, 2006) to calculate the yield strength of the composite filler, and the results showed that the fractional yield stress was increased by 29.7% relative to 0 vol.% WCp while 20 vol.%WCp was incorporated, as shown in Table 1. The plastic deformation ability of brazing alloy in determining the thermal stresses level in a well-bonded joint should not be neglected since it was an important factor to influence the magnitude of the residual stresses (Zhou et al, 1991). At the same time, more cracks or pores occurred in the brazing layer due to poor fluidity of composite filler. The above two factors led to the degradation of bonding strength.

In our previous work, SiCp was incorporated in the brazing alloy to join Si₃N₄ ceramic (He et al, 2010). For convenience, only the Ag-Cu-Ti+SiCp composite filler was utilized to join the Si₃N₄ ceramic, not for ceramic-steel joining. On that basis, the formation mechanism in the joint was clarified, providing guideline for the widely used ceramic-metal joining system. The results indicated that SiCp could react with Ti element during brazing. A definite amount of Ti element was consumed and the amount of Ti element that diffused towards Si₃N₄ ceramic was depressed. For a definite amount of Ti in the composite filler (4wt.%), a thin interfacial reaction layer was thus formed, presenting a bad load-transferring ability and lowering the joint strength. Furthermore, the reaction phases (TiC and

Ti5Si3) between SiCp and brazing alloy possess a larger CTE than that of SiCp, e.g. the CTE for TiC and Ti5Si3 are $8.6 \times 10^{-6} \text{ K}^{-1}$ and $11.0 \times 10^{-6} \text{ K}^{-1}$, respectively, both higher than that of SiCp ($5.2 \times 10^{-6} \text{ K}^{-1}$). Consequently, the effect of CTE reduction was also suppressed. In this investigation, WCp could also interact with Ti during brazing. The difference is that a very thin reaction layer ($\leq 0.1 \mu\text{m}$) was generally formed around WCp. The brazing alloy thus showed good wettability to WCp addition, meanwhile, no excess Ti element was consumed and the reaction phases with high CTE were not precipitated. The above statement was the reason that WCp was selected as the inclusion. The results reported here are expected to provide guidelines for brazing ceramics to metallic parts by using composite filler with different kinds of inclusions.

Different kinds of inclusions were introduced into the joining of ceramic and metal (Zhu et al, 1997; Lin et al, 2007; Yang et al, 2005; Lin et al, 2006). Carbon fiber was the common inclusion and used early. Zhu et al. reported that the addition of short, bare carbon fibers to a silver based active brazing alloy (63Ag-34Cu-2Ti-1Sn) could result in up to 30% improvement in the shear/tensile joint strength between Al₂O₃ and stainless steel (the maximal strength: 116.6 MPa). Lin et al. also introduced Ag-Cu-Ti short carbon fibers as the brazing materials to join carbon fiber-reinforced SiC composite and Ti-alloy, and the maximal shear strength could reach 84 MPa, yet higher than the maximal strength for the case without carbon fiber addition. Yang et al. reported the addition of Al₂O₃ particles to Ag-Cu-Ti brazing alloy for the joining of Al₂O₃ ceramics and investigated the relationship between the interfacial reaction layer growth and brazing time. Lin et al. reported that the Cf/SiC composite was brazed to Ti alloy using interlayer of Ag-Cu-Ti+W mixed powder, and the maximal joint strength could reach 180 MPa while 15 vol.%W was incorporated. In this research, the maximal bending strength of the Si₃N₄ ceramic/42CrMo steel joint could reach 320.5 MPa while 15 vol.% WCp was incorporated, in which the joint strength was 180.65% higher than the strength for the joint without WCp addition. Based on aforementioned analysis, WCp could be powerful in improving the ceramic-metal joint strength. It was believed that the CTE of inclusion and interaction degree between the inclusion and brazing alloy are two critical factors in influencing the joint strength. In addition, the inclusion size and preparation technology of composite filler are also vital on the basis of our work. Especially, the

mechanical alloy method was first used in preparing the composite filler, and it was valuable in achieving the homogenization of each component and eventually strengthening the ceramic-metal joint.

Conclusions

The use of Ag-Cu-Ti+WCp composite filler has successfully led to an increase in the flexural joint strength over the commercially available Ag-Cu-Ti brazing alloy. The following conclusions could be drawn.

The typical structure in the Si_3N_4 /Ag-Cu-Ti+WCp /42CrMo joint was: $\text{Si}_3\text{N}_4/\text{TiN}+\text{Ti}_5\text{Si}_3$ reaction layer/brazing alloy/FeTi+Fe₂Ti reaction layer/42CrMo steel. The brazing alloy was mainly composed of Ag and Cu based solid solution, in which WCp, TiC layer around WC and Cu-Ti intermetallics were dispersed.

With increasing content of WCp, the thickness of reaction layer at the substrates/brazing alloy interface was gradually decreasing. In addition, more Cu-Ti intermetallics were precipitated.

The maximal bending strength was obtained when the joints were brazed with $(\text{Ag}_{72}\text{Cu}_{28})_{96}\text{Ti}_4+15 \text{ vol.}\% \text{WCp}$ composite filler. The following variations occurred in the joint due to WC particles incorporation: CTE reduction of the brazing alloy, formation of Cu-Ti intermetallics, variation of the reaction layer at the Si_3N_4 ceramic/braze interface. The above factors cooperated together to contribute to the maximal joint strength. Over 15 vol.% WCp, the joint strength decreased sharply due to the poor deformation ability and bad fluidity in the brazing alloy.

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